

COMMUNICATIONS

Velocity map imaging studies of the Lyman α photodissociation mechanism for H atom production from hydrocarbons

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H atoms produced in Lyman α photolysis of ethane, propane, and ethylene have been studied using velocity map imaging techniques. Two types of H atoms are identified, one formed along with an alkyl radical in the Rydberg state and the other by the subsequent decomposition of this Rydberg radical. © 1998 American Institute of Physics. [S0021-9606(98)01536-0]

INTRODUCTION

The recent observation of CH₄ and C₂H₆ in Comet C/1996 Hyakutake suggests that saturated hydrocarbons are present in comets and the interstellar medium in addition to being in the atmospheres of the giant planets and their satellites.^{1,2} Thus, it is important to understand the photodissociation processes of these molecules. For the sun and other stars with a similar radiation environment, the most important photodissociation wavelength is Lyman α (121.6 nm), because these saturated hydrocarbons have no appreciable absorption above 140 nm.

There have been many “classical” photochemistry studies of saturated and unsaturated hydrocarbons at Lyman α .^{3,4} Surprisingly, only CH₄ has been studied with modern techniques at 121.6 nm.^{5–7} In this note, preliminary results from the photodissociation of C₂H₆, C₃H₈, and C₂H₄ at Lyman α , using ion imaging techniques to detect and determine the translational energy distribution of H atoms, will be presented. We will show that in the case of the saturated hydrocarbons, the mechanism of dissociation seems to be similar, whereas in ethylene there is a distinct difference.

The imaging apparatus has been previously described⁸ and only the essential elements will be briefly described here. It has a skimmed pulsed molecular beam, which crosses a laser beam in the center of an ion lens used for focusing the image in the time-of-flight apparatus onto the detector. The lens consists of a repeller, an accelerator, and a ground aperture. Its characteristics for imaging studies have been thoroughly documented by Eppink and Parker.⁹ The ground aperture of this lens system serves as the entrance for a 50 cm flight tube that ends with a dual channel plate particle detector and a fast P-47 phosphor. The dual channel plate serves to convert an individual ion to 10⁶ to 10⁷ electrons, which strike the phosphor to provide the final image. This image is recorded with a free running TV camera whose output is digitized and then recorded in a computer, where it can be further processed. A photomultiplier tube is used to

record the total amount of light emitted by the phosphor as a function of time and thus to obtain the time-of-flight (TOF) spectra of the photodissociation fragments. With a known TOF, the input of the dual channel plate detector can be gated so that only the ions of a particular mass will be imaged onto the phosphor and recorded with the TV camera for later processing. Lyman α radiation is generated by four-wave mixing of 364.8 nm laser light in a Kr gas cell that is phase-matched with Ar. The laser light is produced by a Spectra Physics GCR-290-30 Nd-Yag laser pumping a Laser Analytical System LDL 2505 dye laser. The linewidth of the dye laser fundamental was 0.04 cm⁻¹ and the repetition rate was 30 Hz. The H atom images were obtained by scanning the dye laser over the Doppler width of the H atom absorption line, since it is substantially wider than the laser linewidth.

RESULTS AND DISCUSSION

A typical H atom image obtained in these studies is presented in Fig. 1. Images like this were processed using an inverse Abel transform and radial integration over the intensity distribution of recoiling fragments, to obtain H atom translational energy distribution curves, $P(E_T)$.¹⁰ Typical examples of such curves derived from the photolysis of ethane, propane, and ethylene are shown in Fig. 2. What is remarkable about this figure is the similarity between the curves for the two saturated hydrocarbons. The curves are nearly identical, with a peak between 0.2 and 0.3 eV and a tail that extends out of ~ 2.92 to 2.95 eV. This suggests that there may be a common photodissociation mechanism in the Lyman α region for the production of H atoms from the higher alkanes.

Sevin and his co-workers^{11–13} suggested that if the energy of the photolysis photon is high enough, then the production of a H atom and a free radical with the electron in an excited Rydberg orbital will be one of the photochemical channels. The energy of this excited orbital is substantially

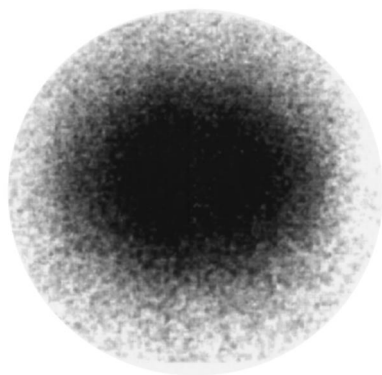
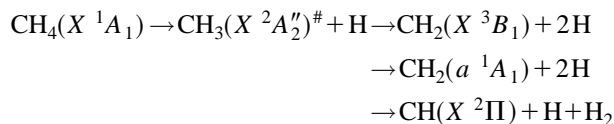


FIG. 1. H atom image formed in the photofragmentation of ethane $\text{C}_2\text{H}_6 + h\nu_{121.6\text{ nm}} \rightarrow \text{C}_2\text{H}_5 + \text{H}$.

above the C–H bond dissociation energy of the radical. Their calculations indicated that the electron in this excited Rydberg orbital collapses to the $1s$ orbital of one of the H atoms in the radical and leads to dissociation of the H atom from the radical. This H atom will have a great deal of translational energy extending to ~ 3.0 eV. The $P(E_T)$ curves of both ethane and propane have H atoms with maximum translational energies, E_T^{max} , out to 2.95 eV, and a most probable translational energy, $\langle E_T \rangle$, of ~ 0.25 eV. The most probable available energy, $\langle E_{\text{avail}} \rangle$, for the internal excitation of the heavy radical fragment, will be given by the following:

$$\langle E_{\text{avail}} \rangle = h\nu_{121.6} - D_0(R-H) - \langle E_T \rangle.$$

Table I gives the $\langle E_{\text{avail}} \rangle$ for the methyl, ethyl, propyl, and vinyl radicals and shows this energy varies from 5.60 to 6.04 eV. The table also lists the C–H bond dissociation energies of the molecules, $D_0(R-H)$ and the radicals, $D_0(M-H)$, as well as the energy of the excited Rydberg state, E_{Ryd}^R . The higher $D_0(R-H)$ and E_{Ryd}^R of the methyl radical mean that



as it has been previously discussed.¹⁴ However, there is not enough available energy to excite the radicals to the first excited Rydberg state unless the methane molecules still have some vibrational energy. The table shows 10.022 eV is needed, and a Lyman α photon only supplies 10.0196 eV. The lowest vibrational frequency in methane is 1306 cm^{-1} , and it is threefold degenerate, so the population at room temperature is only 0.8%. It is unlikely that this small peak is due to CH_4 with one quantum of vibration energy, because it would be smaller unless the Franck–Condon factor is higher than it is for molecules in the ground state with no vibration energy. If vibrational energy is used to supply the required energy for excitation of the CH_3 radical to the $3s$ Rydberg

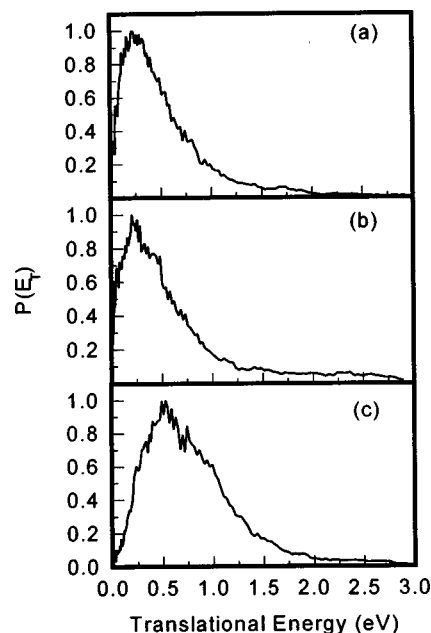


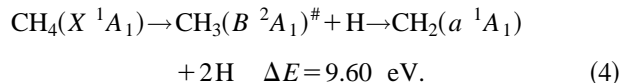
FIG. 2. The $P(E_T)$ derived from the H atom images in the Lyman α photolysis of (a) C_2H_6 , (b) C_3H_8 , and (c) C_2H_4 .

the photolysis of methane at Lyman α cannot lead to excitation of the methyl radical to a Rydberg state. Thus, one would predict methane's $P(E_T)$ for H atoms at Lyman α would be different from the ones observed for ethane and propane. This is consistent with the observations.^{5,6}

A comparison between the $P(E_T)$'s from the earlier imaging experiments on CH_4 and the present ones on ethane and propane shows that they are indeed very different.^{5,6} The $P(E_T)$ for methane has a peak at low kinetic energies similar to the present ones. This means that CH_3 has high internal energy. There is enough energy for further dissociation via the following reactions:



state, i.e., (B^2A_1) , then dissociation would occur, as has been recently demonstrated,¹⁵ via the following:



Using this additional vibrational energy one can provide the needed energy and leave 0.97 eV partitioned between translational and internal energy of the fragments. The CH_2 radical will have no energy left for internal vibration or rotation excitation.

The other peak in the H atom time-of-flight spectra for methane is at 1.5 eV, and it corresponds to lower internal energy in the free radical fragment. This represents the major

TABLE I. Available energy, E_{avail} , at Lyman α 121.6 nm for a free radical fragment, the minimum energy to excite the first Rydberg state of the radical, E_{Ryd}^R , and the (C–H) bond dissociation energies for the molecule, $D_0(R-H)$, and radical, $D_0(M-H)$.

Molecule	$\langle E_{\text{avail}} \rangle$ (eV)	R_{Ryd}	E_{Ryd}^R (eV)	$D_0(R-H)^a$ (eV)	$D_0(M-H)$ (eV)
CH ₄	5.72	CH ₃ [² A ₁ '(3s)] ^{b,c}	5.74	4.48	4.73 ^f
C ₂ H ₆	5.85	C ₂ H ₅ [² A ₁ '(3s)] ^c	5.04	4.35	1.59 ^a
C ₃ H ₈	5.88	<i>n</i> -C ₃ H ₇ [² A ₁ '(3s)] ^d	5.04	4.32	1.48 ^a
C ₃ H ₈	6.04	<i>i</i> -C ₃ H ₇ [² A ₁ '(3s)] ^c	4.59	4.16	1.65 ^a
C ₂ H ₄	5.60	C ₂ H ₃ [² A ₁ '(3s)] ^e	6.25	4.60	1.5–1.6 ^g

^aThe dissociation energies of the radicals were calculated from heats of formation. (See Ref. 22.)

^bReference 14.

^cReference 23.

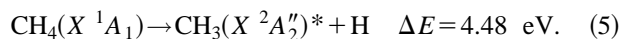
^dReference 24.

^eReference 17.

^fReference 20.

^gReference 25.

channel for the production of H atoms in the Lyman α photolysis of methane.^{5,6} This peak has been assigned to the following process:



More energy has been distributed into translational energy, so there is now not enough available energy for spontaneous fragmentation into another H atom via reactions (1), (2), and (3). If these methyl radicals undergo further dissociation, they will have to dissociate via other reactions with lower energy requirements.^{7,14}

The peak in the $P(E_T)$ curve at 1.5 eV is not observed in the Lyman α photolysis of ethane and propane. The ethyl and propyl radical fragments must then have higher average internal energies than CH₃ radicals produced from the photolysis of CH₄. It is our contention that most of this higher internal energy in the C₂H₅ and C₃H₇ radicals results in the excitation of these free radicals to the lowest Rydberg state. We would expect that the $P(E_T)$ for methane will change to resemble the $P(E_T)$ of ethane and propane when the energy of the photolyzing photon is increased, so that this channel becomes energetically available. There will be a competition between spontaneous dissociation of the CH₃ radical on the excited Rydberg surface and internal conversion of this energy to the ground state surface. This type of competition has recently been observed in the photodissociation of acetylene in the Rydberg region.¹⁶

In ethylene, the excited electronic states have lower energy because of the π electrons in the molecule. Recent work of Mebel *et al.* has shown most of the underlying continuous absorption at 121.6 nm is associated with the π to π^* transition because of the change in geometry.¹⁷ The excitation of the $A(^1B_{1u}) \leftarrow X(^1A_{1g})$ at 121.6 nm is complicated, of course, by mixing with nearby states. However, this state has also been studied at 193 nm, where the other electronic states are not energetically accessible.^{18–20} It was shown that H atom elimination occurred by secondary photodissociation and fragmentation of the vinyl radical in addition to direct photofragmentation. Secondary photodissociation is not a problem in the present work because of the lower photon flux. At 121.6 nm the accessibility of lower energy electronic states will lead to more photochemical channels for H atom

production. Additional studies are needed at different wavelengths to sort out these various dissociation channels.

CONCLUSION

In conclusion, the present work supports the theoretical calculations of Sevin and his co-workers, which suggest that if enough energy is available to form the radicals in a Rydberg state then they will dissociate to produce another H atom.^{11–13} The calculations indicated that H atoms will have a great deal of translational energy which is in agreement with the observed $P(E_T)$ curves. These curves show a low energy peak, which supports the idea of formation of the free radical in a Rydberg state.

While the translational profiles of the H atom are consistent with the proposed photolysis mechanism, there are many questions still to be answered. These include the branching between the detachment of the first H atom and the second H atom and the anisotropy parameters for the parent and daughter dissociation. Precise theoretical curves for the dissociation pathways of the intermediate radicals are also needed. We would also like to identify the heavy products that are the result of the photodissociation process and determine their recoil velocities. Finally, the relative probability for detachment of primary, secondary, and tertiary H atoms from the appropriate starting hydrocarbon compound needs to be determined.²¹ Further studies are currently underway to clarify these and other questions raised by our work.

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